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WORKSHOP ON CHEMICAL WEATHERING ON MARS



MSATT

Mars Surface and Atmosphere Through Time

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WORKSHOP ON
CHEMICAL WEATHERING ON MARS

Edited by
Roger Burns and Amos Banin

Held at
Cocoa Beach, Florida
September 10–12, 1992

Sponsored by
Lunar and Planetary Institute
MSATT Study Group

Lunar and Planetary Institute 3600 Bay Area Boulevard Houston TX 77058-1113

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Program

Thursday, September 10, 1992

8:30 a.m.—12:30 p.m.

Welcoming Remarks

R. G. Burns and A. Banin

CHEMICAL STATE OF THE MARTIAN SURFACE

Clark B. C.

Implications for Volcanogenic Volatile Release on the Weathering of Mars

Zent A. P. McKay C. P.

Chemical Reactivity of the Martian Soil

Bell J. F. III Adams J. B. Morris R. V.

Martian Weathering/Alteration Scenarios from Spectral Studies of Ferric and Ferrous Minerals

Gooding J. L.

Aqueous Geochemistry on Mars: Possible Clues from Salts and Clays in SNC Meteorites

Banin A.

The Mineralogy and Formation Processes of Mars Soil

2:30 p.m.—6:00 p.m.

CLAY SILICATES/PALAGONITES

Bishop J. L. Pieters C. M.

Effects of the Chemical Environment on the Spectroscopic Properties of Clays: Applications for Mars

Orenberg J. B. Handy J. Quinn R.

Reflectance Spectroscopy and GEX Simulation of Palagonite and Iron-rich Montmorillonite Clay Mixtures: Implications for the Surface Composition of Mars

Jenkins T. McDoniel B. Bustin R. Allton J. H.

Effect of Purity on Adsorption Capacities of a Mars-like Clay Mineral at Different Pressures

Newsom H. E.

Chemical Transport During Formation and Alteration of Martian Impact and Volcanic Deposits

Roush T. L.

Infrared Optical Properties of Mars Soil Analog Materials: Palagonites

Burns R. G.

Dehydroxylated Clay Silicates on Mars: Riddles about the Martian Regolith Solved with Ferrian Saponites

7:30 p.m.–9:00 p.m.

WEATHERING EXPERIMENTS AND MODELING I

Mazer J. J. Bates J. K. Bradley C. R.

Preliminary Results of an Experimental Study of the Interactions of Basalt Glass and a Water Vapor Atmosphere: Implications for Weathering on Mars

Moore J. M. Bullock M. A. Stoker C. R.

Mars Brine Formation Experiment

Plumb R. C.

Using the Viking Biology Experimental Results to Obtain Chemical Information About Martian Regolith

Sullivan R.

Weathering Processes Implied from the Analysis of Small Martian Avalanche Chutes

Friday, September 11, 1992

8:00 a.m.–11:45 a.m.

IRON OXIDES/SPECTROSCOPY

Burns R. G.

The Fate of Iron on Mars: Mechanism of Oxidation of Basaltic Minerals to Ferric-bearing Assemblages

Murchie S. Mustard J. Bishop J. Head J. Pieters C. Erard S.

Systematic Variations in the Spectral Properties of Bright Regions on Mars

Geissler P. E. Singer R. B.

An Unusual Spectral Unit in West Candor Chasma: Evidence for Hydrothermal or Aqueous Alteration?

Mustard J. E. Murchie S. L. Erard S. Head J. W.

Composition of Weakly Altered Martian Crust: Clues from Imaging Spectroscopy

Golden D. C. Morris R. V. Ming D. W. Lauer H. V. Jr.
Location of Nanophase Fe-Oxides in Palagonitic Soils: Implication for Martian Pigments

Morris R. V. Golden D. C. Bell J. F. Lauer H. V. Jr. Adams J. B.
Effect of DCB Extraction on Mössbauer and Spectral Data for a Hawaiian Palagonitic Soil (PN-9): Identification of Pigmentary Phases

Koch C. B. Madsen M. B.
Low-Temperature Formation of Magnetic Iron-Oxides

3:00 p.m.–5:00 p.m.

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Plumlee G. S. Ridley W. I. DeBraal J. D.
Chemical Modeling Constraints on Martian Surface Mineralogies Formed in an Early Warm Wet Climate, and Speculations on the Occurrence of Phosphate Minerals in the Martian Regolith

DeBraal J. D. Reed M. H. Plumlee G. S.
Calculated Mineral Precipitation Upon Evaporation of a Model Martian Groundwater Near 0°C

Schaefer M. W.
The Martian Ocean: First Acid, Then Alkaline

Stephens S. K. Stevenson D. J. Keyser L. F.
Experimental Investigation of Carbonate Formation on Mars

7:30 p.m.–9:30 p.m.

SNC METEORITES

Wright I. P. Pillinger C. T. Grady M. M.
Attempt to Comprehend Martian Surface Processes Through Interpretation of the Oxygen Isotopic Compositions of Carbonates in SNC Meteorites

Lal D.
Implications of Isotopic Compositions of N and Ne in the Martian Atmosphere to Temporal Evolution of its Atmosphere and Regolith

Treiman A. H. Barrett R. A. Gooding J. L.
Geochemistry and Setting of Martian (?) "Weathering": The Lafayette Meteorite

Dreibus G. Wänke H.
On the Weathering of Martian Igneous Rocks

Saturday, September 12, 1992

7:30 a.m.—2:00 p.m.

Viewing the shuttle launch at Cape Kennedy.

3:30 p.m.—5:00 p.m.

INFORMAL DISCUSSION AND CONCLUSION

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Summary of Technical Sessions

R. G. Burns and A. Banin

The third MSATT workshop, which was held September 10–12, 1992, at Cocoa Beach/Cape Kennedy, focused on chemical weathering of the surface of Mars. The 30 papers presented at the workshop described studies of martian weathering processes based on results from the Viking mission experiments, remote sensing spectroscopic measurements, studies of the SNC meteorites, laboratory measurements of surface analog materials, and modeling of reaction pathways. Participants at the workshop heard six invited overview lectures and two dozen contributed talks during six scientific sessions that were scheduled during the first two days of the workshop. These presentations, which summarized the current state of knowledge and reported recent research on the chemical evolution of the martian surface, generated many lively discussions among the participants throughout the scientific sessions, particularly during the closing session, which took place after attendees at the workshop had returned from witnessing the launch of the 50th shuttle mission on September 12, 1992.

The Viking Lander experiments performed on the martian surface during 1976–1978 continue to provide a wealth of information about the chemical state and reactivity of the regolith at Chryse and Utopia [1–3]. The XRF measurements, coupled with analyses of the SNC meteorites, account for almost 90 wt% of the martian soil (expressed as oxides of Si, Al, Fe, Mg, Ti, Ca, K, and Na and as sulfate and chloride ions) [1]. The chemical composition of the remaining 10 wt% continues to be debated with various lines of evidence (derived from the Viking biological experiments, studies of SNC meteorites, and remote sensed infrared spectroscopy) suggesting the presence of significant amounts of C (as carbonates [4–7]), P (as phosphates [8,9]), N (as nitrates and peroxy nitrates [2,3]), and H (as OH[−] and water in clay silicates [10–13] that may be partially dehydroxylated [14]). Additional S (as sulfates [1,4,9]) may be present at concentration levels higher than those initially estimated from the Viking XRF analyses of the martian soil [1]. The regolith may also be highly enriched in a number of volatile elements, including F, Br, As, Se, Zn, As, Cu, Br, Sb, Sn, Hg, Pb, and Bi [1,15].

The Viking biological experiments indicated the presence of oxidants in the regolith, and several candidate reactive species have been proposed, including peroxides, peroxy nitrates, and oxyhalides [3]. Simulations of the labeled release experiment may be indicative of iron-enriched clay silicates, which, like the iron oxide phases, appear to be very poorly crystalline [16]. A major question concerning such secondary silicate and iron oxides in the martian soil is why they have not “ripened” into well-crystallized phases [16]. Perhaps water deficiency, low temperatures, and retarded kinetics are responsible for slow weathering reactions of volcanic materials during the recent history of Mars [16,17].

Although the mineralogy of the martian regolith has not been determined directly, a variety of minerals have been proposed based on remote sensing experiments and laboratory investigations of possible analog materials possessing chemical, physical, and spectroscopic properties in common with the martian surface. Predominant among the potential surface alteration products are palagonitic soil, clay silicates, and ferric oxides.

Clay minerals continue to be extensively studied as surface analogs with most attention centering on Fe^{3+} -bearing montmorillonite and nontronite [10,11,13,16,18]. However, attention was drawn to the presence of iron saponites on Mars, based on evidence of deep-weathering of terrestrial igneous rocks [14], reported occurrences in SNC meteorites [4,19], and experimental hydrothermal alteration product of basalts [20]. By analogy with terrestrial occurrences, hydroxyl-deficient or dehydroxylated ferrian saponites may exist on Mars [14], accounting for relatively weak O-H infrared spectral features in remote sensed spectra. The cation adsorption properties [10,16], CO_2 uptake [21], and spectral features [10,11,13,14] of clay silicates are being studied by several participants. Iron-exchanged montmorillonite containing ferric oxides as surface or interlayer species continues to be a popular candidate for several spectral features of Mars [10,16], as well as a potential reactive substrate that influenced the Viking biological experiments [13,16]. However, the identity of the interlayer ferric oxide is still debated [14,16], with ferrihydrite, lepidocrocite, and nanophase hematite being possible constituents. Measurements of adsorption capacities of clays have shown that CO_2 adsorption increases in nontronite devoid of water, so that the martian regolith could function as an effective reservoir of CO_2 [21]. In infrared spectra of ferric montmorillonites subjected to arid environments, the 1.9- μm band is weaker than the 2.2- μm band [10,11,13]. Moreover, reflectance spectra of palagonite-montmorillonite mixtures indicate that a threshold limit of about 15% montmorillonite is required before the diagnostic 2.2- μm band becomes conspicuous [13]. Thus, ferric montmorillonite may be present as a major constituent of the regolith, but be difficult to identify in remote sensed spectra of the martian surface [10,13].

Palagonite, formed as an alteration product of basaltic glass, is considered by many participants to be a terrestrial analog of bright regions on Mars [13,15,18,20,22,23], based on the spectral properties in the visible [18,22,24] and midinfrared regions [13,23], studies of impact crater deposits [15], and reaction products in hydrothermal experiments [20]. Studies of midinfrared spectra indicate that terrestrial palagonites generally fall into two categories based on Si-O vibrations around 1000 cm^{-1} [23]. One implication of this result for interpreting thermal infrared data during the forthcoming Mars Observer mission is that only a limited number of terrestrial analogs need to be considered [23]. Pigmentary ferric oxides consisting of nanophase hematite with minor bulk hematite were identified in Hawaiian palagonitic soils, a spectral analog of martian regolith, based on Mössbauer and reflectance spectral data of soils before and after extraction of nanophase ferric oxides with dithionate-citrate-bicarbonate solutions [18]. Transmission electron microscopy studies of palagonitic soils [4], as well as hydrothermally altered basaltic glass [20], suggest that chemical weathering reactions proceeded by removal of soluble cations and Si followed by the precipitation of a smectite or zeolite away from the glass weathering front, while leaving a residue of nanophase iron oxides [4]. Mössbauer spectroscopy also identified nonstoichiometric magnetite that had formed in cracks, rather than exposed surfaces, during low-temperature terrestrial weathering of basaltic rocks [25].

Remote sensed reflectance spectra continue to serve as constraints for candidate ferric oxides and clay silicates in bright regions of Mars [11,24,26], as well as identifying ferromagnesian silicates in relatively unoxidized dark regions of the surface [12]. An unusual spectral unit in the central Valles Marineris appears to be hematite rich, but may also contain ubiquitous nanophase ferric oxide [26]. The unit may result from volcanic activity and circulating hydrothermal fluids or be a weathered ore deposit [17,26]. Multispectral imaging data returned from the ISM instrument on the Phobos 2 mission are indicative of variability of water-, hydroxyl-, and ferric-bearing phases in bright reddish regions of Mars [11,12]. There are indications that older deposits that formed when Mars had a wet, warm climate may differ from

younger deposits originating when the surface of the planet was cooler [12]. Thus, although ferric oxides and inferred altered materials are widespread on Mars, the ISM data confirm that in darker regions the surface of the planet is relatively fresh [12]. Basaltic rocks with a weakly altered, low-albedo crust correlate with the ISM measurements, which indicate pyroxene compositions consistent with augite-pigeonite assemblages or chemically zoned pyroxenes with a similar bulk composition [12].

Investigations of carbonates on Mars have been motivated by attempts to establish sinks for CO_2 , the atmospheric pressure of which is generally believed to have been higher during past warmer climates on Mars. Geochemical cycle models for the atmosphere-hydrosphere-regolith system on Mars have been computed [5]. In preliminary models excluding changes of water volume and salinity, the calculations suggest that atmospheric CO_2 passed rapidly through the oceans to form carbonate deposits and that after about 10^4 yr a sharp drop of CO_2 pressure occurred and was associated with increased alkalinity of the oceans [5]. Experiments studying rates of removal of atmospheric CO_2 by powdered diopside in the absence of liquid water indicate that CO_2 storage proceeds rapidly enough to get rid of 1 bar CO_2 in 10^4 to 10^5 yr [6]. Dry mass wasting considered to be responsible for the recession of the walls of Valles Marineris could result from decreased cohesion energies of subsurface materials by sublimation of ice into the atmosphere [27].

Computer-based reaction-path calculations for chemical processes that might have occurred during a postulated early warm, wet climate on Mars set constraints on the chemistry of rainwater and rainwater-basalt interactions [9]. Rainwater in equilibrium with atmospheric $P_{\text{CO}_2} = 2.2$ bar and $P_{\text{O}_2} = 10^{-5}$ bar would have a pH of about 4.08 (cf. pH = 5.66 under higher P_{O_2} and lower P_{CO_2} currently on Earth). Addition of volcanic gases lowers the pH and raises the amount of dissolved sulfate and chloride [9]. Interactions of such acidic rainwater with Chassigny parental magma initially produces ferric and Mn oxyhydroxides, kaolinite, smectites, chalcedony, and apatite at high water-rock ratios (>100) and low pH values [9]. As more basalt reacts with the rainwater, the pH increases to near 8 for smaller water-rock ratios (<10) and dolomite and calcite are predicted to form, together with ferrihydrite, apatite, and smectites, once kinetic barriers to nucleation are overcome. Limited evaporation of water that had previously reacted with basalt produces gypsum, calcite, dolomite, alkali feldspars, and phosphate minerals [9]. Similar calculations of minerals precipitated from groundwater buffered by the present-day martian atmosphere indicate that dolomite, quartz, dawsonite $[\text{NaAlCO}_3(\text{OH})_2]$, and nontronite saturate at the beginning of the evaporation [28]. After 65% evaporation they are joined by gypsum, which is replaced by anhydrite once 99.8% of the water has evaporated. Since alkali chlorides have not yet precipitated at this point, Cl^- ions produced by weathering of basalt could be accommodated, instead, in apatite [8,28].

Rates of chemical weathering of Fe^{2+} -bearing minerals on Mars are predicted to be strongly dependent on pH as well as temperature, ionic strength, and concentration of dissolved oxygen [17]. In acidic groundwater, silicate minerals dissolve rapidly, but oxidation rates of aqueous Fe^{2+} ions are very slow, particularly in brines at low temperatures. At near-neutral pH, oxidation rates of dissolved Fe^{2+} increase, but dissolution rates of ferromagnesian silicate minerals decrease. As a result, rates of oxidative weathering on the present-day surface of Mars are estimated to be 10^6 times slower than they were in the past when a warm, wet climate probably prevailed [17]. Experimental studies of interactions of basalt glass with atmospheric water vapor under maximum humidity and at elevated temperatures indicate that smectite clay (saponite) forms on outermost surfaces of the glass [20]. Between the clay and unreacted glass is an amorphous gel-like (palagonite) phase [20]. Extrapolation to 0°C yielded an alteration rate of about

0.05 μm per year [20], which may be higher than reaction rates on the present-day surface of Mars where atmospheric water vapor is considerably lower.

Experiments to identify soluble salts and compositions of martian brines are being made using mineral mixtures that simulate assemblages in SNC meteorites [29]. In leaching experiments performed on samples of SNC meteorites [8], the bulk of Cl and Br, and much of the Na and K, is water-leachable in Nakhla. Smaller proportions of these ions were water-leached from Shergotty, but were completely extracted by dilute acid. The leaching experiments revealed differences of behavior of REE elements and for U relative to K, suggesting that the U and the REE elements, but not K, are accommodated in acid-soluble apatite [8].

The question of chemical transport associated with alteration of impact melts on Mars has been addressed by examining hydrothermal alteration products of palagonites associated with volcanic and impact deposits [15]. Chemical clues have been sought to distinguish between volcanic vs. impact crater sources of the martian soil and alteration processes under ambient conditions vs. hydrothermal conditions. Limited data indicate slight enrichments of Fe and Al in altered impact material and slightly increased transport of volatile elements in impact melt deposits compared to fumarolic deposits [15].

Studies of SNC meteorites have provided clues to the chemical environment beneath the martian regolith in which authigenic minerals were formed by groundwater-basalt interactions [8,4,7,19]. All subgroups of SNC meteorites contain traces of water-precipitated minerals, including various combinations of carbonates, sulfates, halides, ferric oxides, and clay silicates [4]. Inferences from these mineral assemblages are that they were associated with saline aqueous solutions that were oxidizing and alkaline [4]. Temperatures of the pore waters are not so well constrained, but were probably below 70°C. In Lafayette, several generations of cross-cutting rusty veinlets of aqueous alteration material (composed of saponite plus ferrihydrite) replacing olivine are observed, indicating episodic water flow or injection [19]. The preterrestrial origin of the alteration materials is shown by textural and mineralogical changes of the veinlets toward the exterior fusion crust [19]. Carbonates in EETA 79001 and Nakhla have similar carbon and oxygen stable isotopic compositions suggestive of a common (martian) origin [7]. There are also some similarities to Antarctic weathering products, suggesting comparable equilibration temperatures with water on the two planets [7]. The water and acid leaching studies of SNC meteorites also correlate with the formation of aqueous alteration products on Mars [8]. The SNC meteorites may also hold the key to identifying cosmogenic ^{15}N formed in the regolith of Mars [30].

In summary, the ongoing research discussed at the workshop demonstrated that planetary geochemists are gaining fresh insights into the processes and products of chemical weathering reactions on Mars. However, major questions still remain concerning thermodynamic equilibria and chemical kinetics of soil-forming processes by rock-water and rock-atmosphere interactions. Definitive answers to these questions will require well-coordinated experimental investigations, computations of reaction pathways, *in situ* and remote sensing observations, and future sampling missions to Mars in order to determine the extent of surface alteration processes and to identify the secondary minerals that have formed during chemical weathering of volcanic rocks on the martian surface.

References: Abstracts of papers presented at the Workshop on Chemical Weathering on Mars, which appear in LPI Technical Report Number 92-04, Part 1.

- [1] Clark B. C., *Implications for Volcanogenic Volatile Release on the Weathering of Mars*. [2] Plumb R. C., *Using the Viking Biology Experimental Results to Obtain Chemical Information About Martian Regolith*. [3] Zent A. P. and McKay C. P., *Chemical Reactivity of the Martian Soil*. [4] Gooding J. L., *Aqueous Geochemistry on Mars: Possible Clues from Salts and Clays in SNC Meteorites*. [5] Schaefer M. W., *The Martian Ocean: First Acid, Then Alkaline*. [6] Stephens S. K., Stevenson D. J., and Keyser L. F., *Experimental Investigation of Carbonate Formation on Mars*. [7] Wright I. P., Pillinger C. T., and Grady M. M., *Attempts to Comprehend Martian Surface Processes Through Interpretation of the Oxygen Isotopic Compositions of Carbonates in SNC Meteorites*. [8] Dreibus G. and Wänke H., *On the Weathering of Martian Igneous Rocks*. [9] Plumlee G. S., Ridley W. I., and DeBraal J. D., *Chemical Modeling Constraints on Martian Surface Mineralogies Formed in an Early, Warm, Wet Climate, and Speculations on the Occurrence of Phosphate Minerals in the Martian Regolith*. [10] Bishop J. L. and Pieters C. M., *Effects of the Chemical Environment on the Spectroscopic Properties of Clays: Applications for Mars*. [11] Murchie S., Mustard J., Bishop J., Head J., Pieters C., and Erard S., *Systematic Variations in the Spectral Properties of Bright Regions on Mars*. [12] Mustard J. F., Murchie S. L., Erard S., and Head J. W., *Composition of Weakly Altered Martian Crust: Clues from Imaging Spectroscopy*. [13] Orenberg J. B., Handy J., and Quinn R., *Reflectance Spectroscopy and GEX Simulation of Palagonite and Iron-rich Montmorillonite Clay Mixtures: Implications for the Surface Composition of Mars*. [14] Burns R. G., *Dehydroxylated Clay Silicates on Mars: Riddles about the Martian Regolith Solved with Ferrian Saponites*. [15] Newson H. E., *Chemical Transport During Formation and Alteration of Martian Impact and Volcanic Deposits*. [16] Banin A., *The Mineralogy and Formation Processes of Mars Soil*. [17] Burns R. G., *The Fate of Iron on Mars: Mechanism of Oxidation of Basaltic Minerals to Ferric-bearing Assemblages*. [18] Morris R. V., Golden D. C., Bell J. F. III, Lauer H. V. Jr., and Adams J. B., *Effect of DCB Extraction on Mössbauer and Spectral Data for a Hawaiian Palagonitic Soil (PN-9): Identification of Pigmentary Phases*. [19] Treiman A. H., Barrett R. A., and Gooding J. L., *Geochemistry and Setting of Martian(?) "Weathering": The Lafayette Meteorite*. [20] Mazer J. J., Bates J. K., and Bradley C. R., *Preliminary Results of an Experimental Study of the Interactions of Basalt Glass and a Water Vapor Atmosphere: Implications for Weathering on Mars*. [21] Jenkins T., McDoniel B., Bustin R., and Allton J. H., *Effect of Purity on Adsorption Capacities of a Mars-like Clay Mineral at Different Pressures*. [22] Golden D. C., Morris R. V., Ming D. W., and Lauer H. V. Jr., *Location of Nanophase Fe-Oxides in Palagonitic Soils: Implication for Martian Pigments*. [23] Roush T. L., *Infrared Optical Properties of Mars Soil Analog Materials: Palagonites*. [24] Bell J. F. III, Adams J. B., and Morris R. V., *Martian Weathering/Alteration Scenarios from Spectral Studies of Ferric and Ferrous Minerals*. [25] Koch C. B. and Madsen M. B., *Low-Temperature Formation of Magnetic Iron-Oxides*. [26] Geissler P. E. and Singer R. B., *An Unusual Spectral Unit in West Candor Chasma: Evidence for Hydrothermal or Aqueous Alteration?* [27] Sullivan R., *Weathering Processes Implied from Analysis of Small Martian Avalanche Chutes*. [28] DeBraal J. D., Reed M. H., and Plumlee G. S., *Calculated Mineral Precipitation Upon Evaporation of a Model Martian Groundwater Near 0°C*. [29] Moore J. M., Bullock M. A., and Stoker C. R., *Mars Brine Formation Experiment*. [30] Lal D., *Implications of Isotopic Compositions of N and Ne in the Martian Atmosphere to Temporal Evolution of Its Atmosphere and Regolith*.

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